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A review on phase change materials integrated in building walls

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ABSTRACT

The present paper is the first comprehensive review of the integration of phase change materials in building walls. Many considerations are discussed in this paper including physical considerations about building envelope and phase change material, phase change material integration and thermophysical property measurements and various experimental and numerical studies concerning the integration. Even if the integrated phase change material have a good potential for reducing energy demand, further investigations are needed to really assess their use.

Contents

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1. Introduction

As demand in thermal comfort of buildings rise increasingly, the energy consumption is correspondingly increasing. For example, in France, the energy consumption of buildings has increased by 30% during the last 30 years. Housing and tertiary buildings are responsible for the consumption of approximately 46% of all energies and approximately 19% of the total CO_2 emissions [1]. Nowadays, thermal energy storage systems are essential for reducing dependency on fossil fuels and then contributing to a more efficient environmentally benign energy use [2].

Thermal energy storage can be accomplished either by using sensible heat storage or latent heat storage. Sensible heat storage has been used for centuries by builders to store/release passively thermal energy, but a much larger volume of material is required to store the same amount of energy in comparison to latent heat storage. The principle of the phase change material (PCM) use is simple. As the temperature increases, the material changes phase from solid to liquid. The reaction being endothermic, the PCM absorbs heat. Similarly, when the temperature decreases, the material changes phase from liquid to solid. The reaction being exothermic, the PCM desorbs heat. The integration of PCM in building walls is a way to enhance the storage capacity of building envelope and then to rationalize the use of renewable and non-renewable energies.

The number of articles concerning the PCM integration in building walls (PCMIBW) has increased during the last five years. Then, this paper is dedicated to a review of such PCMIBW. So, Section 2 deals with a factual analysis of the papers from the literature. Some physical considerations concerning PCMIBW and heuristic arguments are given in Section 3. Section 4 deals with some basics of phase change theory which is very important for the understanding of heat transfers. A review of PCM studied in the literature is developed in Section 5. The integration of PCM highly depends on the containment, and then Section 6 deals with this specific problem. Section 7 deals with the measurement of PCM and PCMIBW thermophysical properties. Sections 8 and 9 of the paper are respectively dedicated to a review of experimental and numerical studies concerning PCMIBW.

2. Source of articles and categories

2.1. Source of articles

Conference papers have been voluntarily omitted to avoid any duplications. Fig. 1 shows the distribution of the number of articles since 1979. Three phases can be distinguished: around 1980, between 1990 and 2000 and after 2003. The first studies dealing with PCM integration into building walls are dated from the 80s (3 publications). Then, during the period between 1980 and 1990, only 2 articles have been published. From 1990 to 2000, the number of publications per year increases to about 1 publication per year. After 2003, an increase in the number of publications occurred (reaching up to 14 articles). Almost 80% of the studies have been carried out over the past 8 years which have seen the development of new encapsulation technologies and new energy standards. However, this analysis should take into account the fact that the number of articles per journal has increased significantly since 1979.

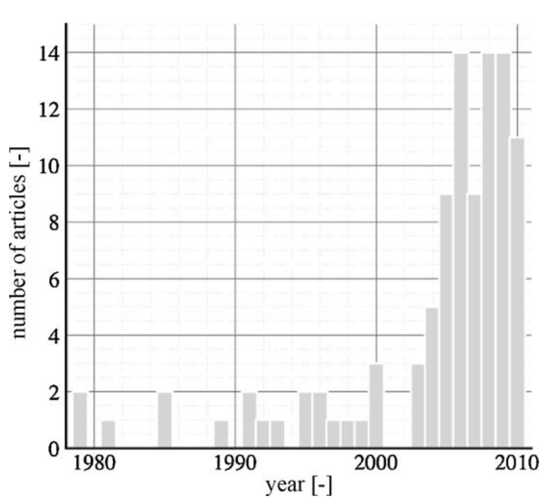


Fig. 1. Evolution of the number of publications since 1979.

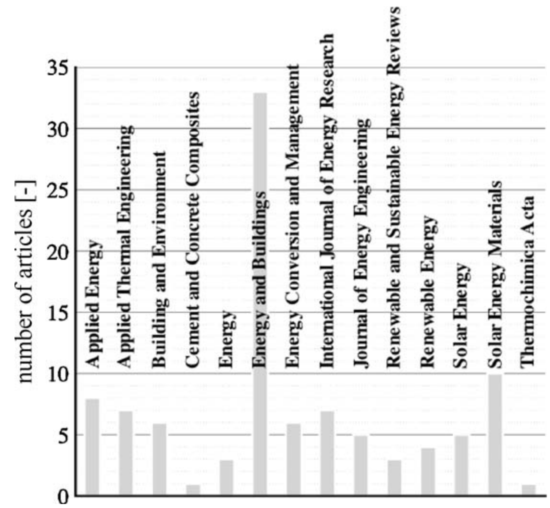


Fig. 2. Distribution of the publications per journal.

Fig. 2 presents the distribution of the studies per journal. Most of the publications (51%) come from 3 journals. Furthermore, almost 85% of the articles have been published by the same publisher.

As an example, the journal shown in Fig. 2 that published 33 articles, has multiplied by 4.3 the number of papers published between 1979 (38 papers) and 2009 (164 papers). The same kind of observation can be made for the other journals. Finally, it is possible to conclude that interest in the subject rising, because the number of publications has risen by a factor of 12.

The distribution of the publications per country is shown in Fig. 3. The origin of the articles can be diverse depending on the

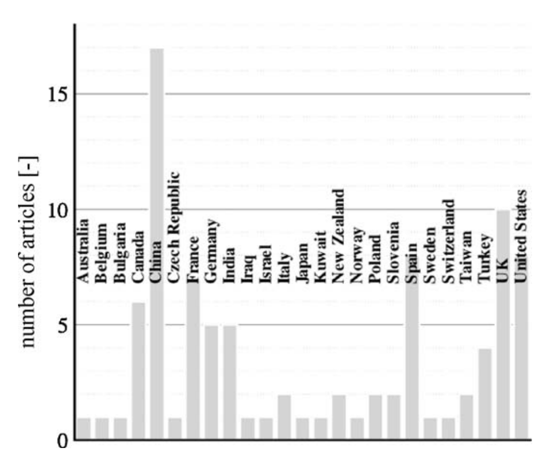


Fig. 3. Number of publications per country.

authors' affiliation. As a consequence, the total number of studies in Fig. 3 is greater than the total number of articles collected in this paper (99 articles but all of them are not cited in the present paper). More than 17% of the articles have been published by China.

2.2. Categories of articles

The review articles represent about 10% of the total amount of papers (9 review articles [3–11]). All of these articles deal with the general problem of thermal energy storage using PCM and no only the case of PCM walls.

Removing the review articles from the list, the identified categories concerning the publications are as follows:

- 41% of publications deals only with experimental studies; 26% of these papers are dedicated to the development and evaluation of PCM walls only.
- 38% of publications are dedicated to the numerical evaluation of PCM walls.
- 21% of the publications deal with both experiment and numerical modeling.

It is interesting to note that no study, experimental or numerical, examines the evaluation of PCM walls in real conditions, i.e. with internal loads.

3. Integration of PCM in building envelope: physical considerations and heuristic arguments

3.1. Physical considerations

The building is a quite complex object submitted to internal and external solicitations (see Fig. 4). External solicitations are due to the local external weather. Internal solicitations come from solar radiative flux entering the building and internal loads. A high-energy efficiency building must have an energy efficient envelope that can ensure comfort of occupants with a minimum system energy requirement. From this point of view, thermal energy storage in the envelope is a key factor.

Inside a building room, the heat transfer processes between the surface of the wall and the solicitations are as follows:

- convective heat transfer between the air and the surface,
- shortwave radiative heat transfer,
- longwave radiative heat transfer.

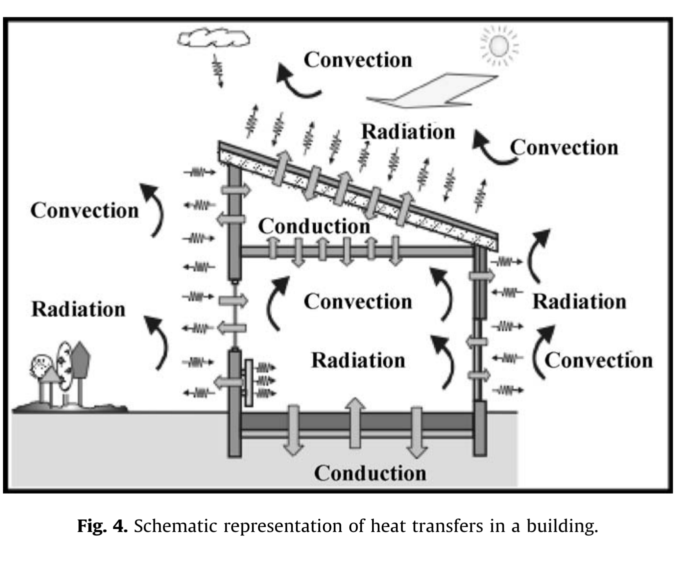


Fig. 4. Schematic representation of heat transfers in a building.

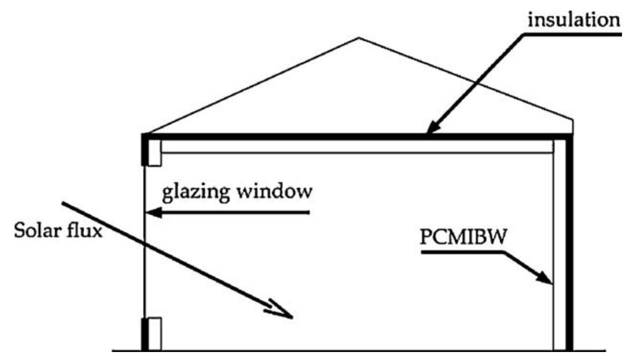


Fig. 5. A schematic representation of PCMIBW in a house with solar gain.

The heat transfer in the wall is conduction. Outside the envelope, the heat transfer processes are the same as inside the building room.

The effect of thermal energy storage in the building envelope is to reduce the indoor temperature fluctuations and to delay the air temperature extremum. Thermal energy is usually stored in the building envelope by sensible heat of the materials. The storage capacity is related to the mass-specific heat capacity and the mass of the materials used in the building envelope. Of course, the storage capacity of the envelope is also related to the composition of the walls and the technological solutions. For example, a wall composed of concrete with external insulation has a higher storage capacity than the same wall with internal insulation.

For example, lightweight buildings have low thermal energy storage capacity because of the materials used for the envelope. In that case, integration of PCM enhances the storage capacity (see Fig. 5): as the temperature increases, the material changes phase from solid to liquid and the PCM absorbs heat. Similarly, when the temperature decreases, the material changes phase from liquid to solid and the PCM desorbs heat. PCM can also be used to control the air temperature: contrary to sensible heat storage, latent heat storage occurs at the phase change temperature without a significant raise in temperature.

On the whole, a high-energy efficient building envelope must have the following characteristics:

- few thermal energy losses with the exterior by thermal insulation,
- use of renewable energy using for example sun radiation through glazing windows,
- limitation of overheating or energy demand peaks using PCMIBW.

3.2. Heuristic arguments

Using very simplified assumptions, Peippo et al. [12] presented approximate formulae for optimum phase change temperature and thickness of the PCMIBW:

$$T_{m,opt} = \overline{T}_r + \frac{Q}{ht_{stor}} \quad (1)$$

$$D_{opt} = \frac{t_n h}{\rho \Delta H}(T_{m,opt} - T_n) \quad (2)$$

$$\overline{T}_r = \frac{t_d T_d + t_n T_n}{t_d + t_n} \quad (3)$$

where $T_{m,opt}$ is the optimal phase change point of the PCM (°C), T_r is the average room temperature (°C), Q is the heat absorbed by unit

area of the room surface (J/m^2), h is the average heat transfer coefficient between wall surface and surroundings (W/m^2/K), T_d is the room daytime temperature (°C), T_n is the room nighttime temperature (°C), t_d is the charging time, day (s), t_n is the discharging time, night (s), t_{stor} is the diurnal storage, cycle = $t_d + t_n$ (s) (24 h), D_{opt} is the optimal thickness of the PCM slab (m), ΔH is the latent heat of fusion of PCM (J/kg).

The previous formulae are very simplified and cannot be used to optimize a PCM wall used in a building. For example, the optimal thickness of the wall highly depends on the thermal diffusivity of the PCM composite. The reason is that the penetration time for transient heat conduction t_p can be evaluated by [13]:

$$t_p \approx \frac{(e/2)^2}{\alpha} \tag{4}$$

where α is the thermal diffusivity of the medium (m^2/s) and e the thickness of the wall (m). Of course, the penetration time must have a value lower than 12 h if diurnal heat storage is required.

4. Phase change theory

From a practical point of view, only the phase change solid–liquid is used in building envelope. The material can be a pure substance, an eutectic mixture or a non-eutectic mixture. The difference between eutectic and non-eutectic mixture is the phase change temperature: for an eutectic mixture, the phase changes at a constant temperature whereas, for a non-eutectic mixture, the phase changes during a temperature interval. From the literature review, the phase change materials used have phase change temperature in the range (20 °C, 60 °C).

4.1. The phase change of a pure ideal body

The exact definition of the phase of a pure body is "an area in the space of the thermodynamic parameters (T,p,V) of a system composed uniquely of the pure body, in which the free energy is an analytical function".

Let us consider the volume V of the system fixed. The areas occupied by each phase can be represented in a plan of which the abscissa is the temperature T and the ordinate is the pressure p. This representation is commonly called the phase diagram, an example is drawn in Fig. 6. There are three phases on the diagram. When the pure body is at the thermodynamic equilibrium with a pressure p_0 and a temperature T_0, its phase is the phase 2.

The matter can be found under several states. The three most common states are gas, liquid and solid. Generally, the state of the matter corresponds directly to phase, that is why the terms "solid phase", "liquid phase", and "gas phase" are usually used.

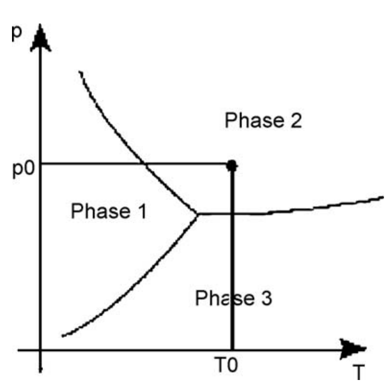


Fig. 6. Phase diagram.

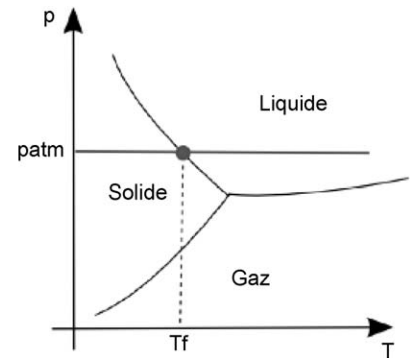


Fig. 7. Equilibrium areas of the liquid and solid phases at the atmospheric pressure.

The phase change, which is usually used to store latent heat energy in buildings, is between the liquid phase of the material and its solid phase. The liquid → solid transformation is called solidification and the solid → liquid transformation is called fusion.

The pressure can be considered as constant during the phase change in building applications; its value being equal to the atmospheric pressure p_{atm}. If a transformation corresponding to a constant pressure $p = p_{atm}$ (horizontal line in Fig. 7) is drawn on the phase diagram, this line intercepts the liquid–solid boundary. The temperature at this crossing is called the fusion temperature of a pure body. If $T \leq T_f$, the pure body at the thermodynamic equilibrium is solid. If $T \geq T_f$, the pure body at the thermodynamic equilibrium is liquid.

Now let us consider the phase change dynamics. The pure body is subjected to a temperature perturbation at a time t, it reaches its thermodynamic equilibrium at a time $t + \Delta t$. The change in thermodynamic equilibrium is mainly due to heat exchanges with the external environment. The time for the pure body to reach the new thermodynamic equilibrium is the time needed for the heat to be exchanged.

Fig. 8 shows the time evolution of the temperature T of the pure ideal body, and the time evolution of the heat flux q leaving the body, if the external environment is subjected to a temperature step ΔT, which leads to the solidification of the body. During the cooling there are three steps:

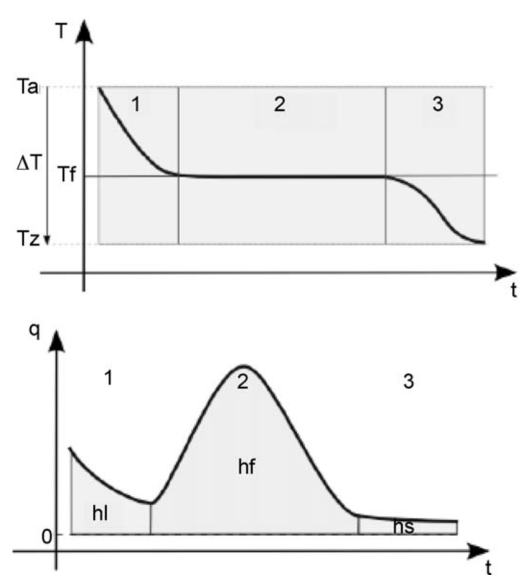


Fig. 8. Time evolution of the temperature and heat flux during the solidification of a pure body submitted to a temperature step ΔT.

1. *The cooling of the liquid*: The pure liquid body releases sensible heat and its temperature decreases until it reaches the temperature of fusion. The total amount of energy released is equal to $h_l = C_{p_l}\int_{T_f}^{T_a} dT$ where C_{p_l} is the heat capacity of the liquid phase. h_l corresponds to the area under the heat flux curve.
2. *The phase change*: The latent heat is released. The temperature remains constant.
3. *The cooling of the solid*: The pure solid body releases sensible heat and its temperature decreases until it reaches the equilibrium temperature. The total amount of energy released is equal to $h_s = C_{p_s}\int_{T_z}^{T_f} dT$ where C_{p_s} is the heat capacity of the solid phase.

The curves of Fig. 8 depended on the thermal solicitation due to a modification of the external environment. When such a curve has to be examined, it is important to know the nature of the thermal solicitation. The most frequent graphics found in the literature are:

- *Temperature step response*: The time evolution of the material's temperature due to an external temperature step (Fig. 8).
- *Temperature scanning response*: The evolution of the released heat flux as a function of the external temperature T_{ext}, when this temperature is following a ramp (scanning) (Fig. 9). Thus, the curve depends on the speed of the external temperature increase.

The latent heat of the material is obtained from the area under the curve and the external temperature speed $V_{T_{ext}} = dT_{ext}/dt$, which is constant. The latent heat is deduced from the formula:

$$h_f = \int_{t_1}^{t_2} q(t)dt = \int_{T_e}^{T_0} q(T_{ext})\frac{\partial t}{\partial T_{ext}}dT_{ext} = \frac{1}{V_{T_{ext}}}A_f \quad (5)$$

Then, some characteristic temperatures are necessary to enable quantitative comparison between different curves:

- T_i and T_f: initial and final temperatures respectively at the beginning and the end of the deviation from the sensible heat transfer curve.
- T_p: peak temperature of the maximum heat flux.
- T_o and T_e: On each side of the maximum heat flux point, there is an inflexion of the curve. Tangents lines can be drawn at the inflexion points. Those temperatures are the temperatures at the intersection between the tangents ant the base of the curve i.e. onset temperature T_o and end temperature T_e.

The most commonly used temperatures to get the characteristics of a PCM are T_p, T_o, and $\Delta T = T_o - T_e$, the width of the peak.

The solidification of a PCM begins with a nucleation effect. The nucleation is the formation of initial crystals, called nucleus. Then, the crystals propagate in the material to form the solid phase. The nucleation rate of a material is its capability to produce nucleus when the temperature decreases below the fusion temperature. If the nucleation rate of a material is too low, it can remain in the liquid phase when its temperature decreases below the fusion temperature. The solidification starts later: the material temperature rises again suddenly to the phase change temperature, as shown in Fig. 10. This effect is called the supercooling effect and is very important when dealing with pure PCM.

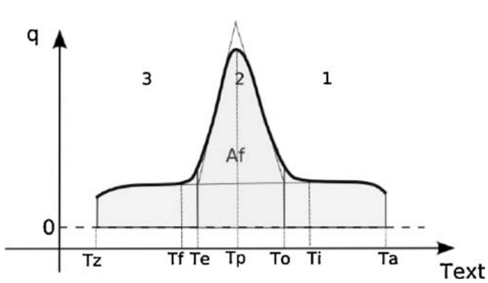


Fig. 9. Heat flux profile of a temperature scanning response.

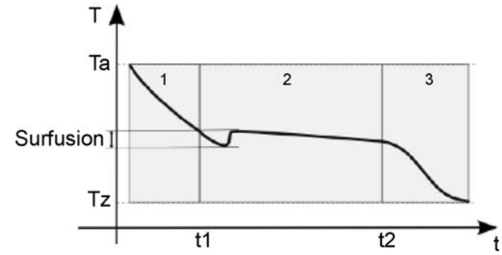


Fig. 10. Supercooling effect.

4.2. The phase change of a mixture

This section is devoted to the physical description of the phase change of a binary mixture. Of course, for multi-components mixture, the theory is quite similar but more complicated from a representation point of view. The binary diagram is used to represent the location of the different phases of a mixture.

Fig. 11 shows a binary diagram of an isomorphous system. The abscissa corresponds to the proportion of the component B in the mixture $A + B$, and the ordinate is the temperature of the mixture. The volume and the pressure are constant.

The diagram consists of two single-phase fields separated by a two-phase field. The boundary between the liquid field and the two-phase field in Fig. 11 is called the liquidus; that between the two-phase field and the solid field is the solidus. In general, a liquidus is the locus of points in a phase diagram representing the temperatures at which mixtures of the various compositions of the system begin to freeze on cooling or finish melting on heating; a solidus is the locus of points representing the temperatures at which the various mixtures finish freezing on cooling or begin melting on heating. The phases in equilibrium across the two-phase field (the liquid and solid solutions) are called conjugate phases.

Let us take the example of a binary mixture composition represented by line (I). If the mixture is solid and the temperature increase, the melting begins at the temperature T_h (i.e. point h) and the composition is totally liquid at temperature T_c (i.e. point c). If

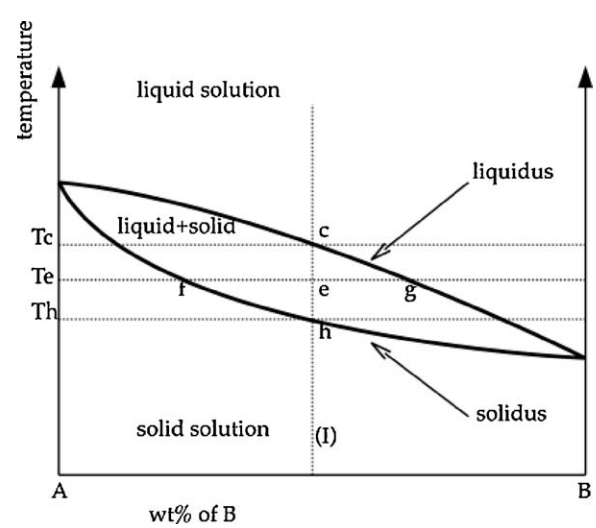


Fig. 11. Binary phase diagram – isomorphous system.

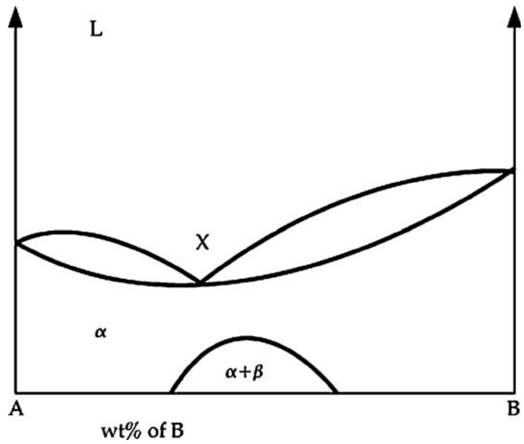


Fig. 12. Binary phase diagram – azeotropic point.

the mixture is liquid and the temperature decrease, the solidification begins at the temperature T_c (i.e. point c) and the composition is totally solid at temperature T_h (i.e. point h). There is a hysteresis phenomenon in the phase change.

If the mixture is at temperature T_e (i.e. point e), the composition of the mixture is given by the location of points f and g:

$$\frac{\overline{eg}}{\overline{fg}} \times 100\% = \% \text{ of solid present} \tag{6}$$

$$\frac{\overline{fe}}{\overline{fg}} \times 100\% = \% \text{ of liquid present} \tag{7}$$

Depending on the components, several phase diagrams exist depending on the phase change behaviour of the mixture. Fig. 12 shows the phase diagram with a large solubility gap and a minima liquidus temperature, e.g. an azeotropic point X.

Fig. 13 shows the special case of a system with an eutectic mixture i.e. point E; it is a mixture at such proportions that melting point is as low as possible and that all the components crystallize simultaneously.

Fig. 14 extract from [14] shows the experimental phase diagram of binary mixtures system of $C_{14}H_{30}$ and $C_{16}H_{34}$. The eutectic point M of the mixture occurs at 91.67% of tetradecane, and the phase change temperature at this point is approximately 1.7 °C. Of course, the phase diagram is necessary to correctly model the heat stored/release but, presently, it is never used for building simulations.

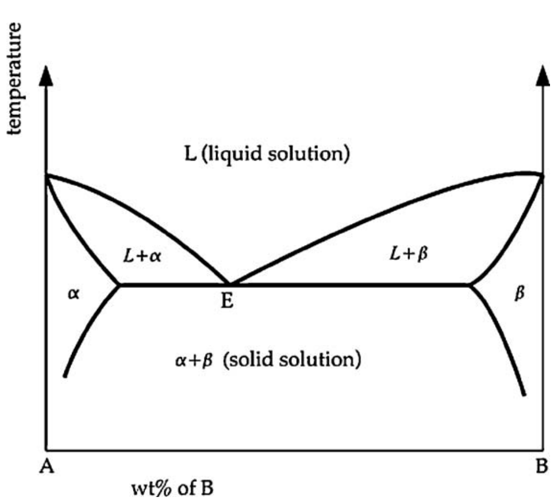


Fig. 13. Binary phase diagram – eutectic point.

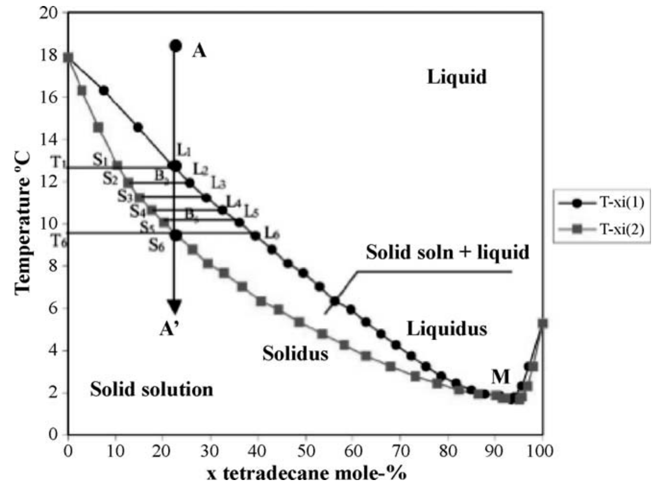


Fig. 14. The liquid–solid phase diagram of binary mixtures system of $C_{14}H_{30}$ and $C_{16}H_{34}$ from [14].

5. Phase change materials used in building walls

The phase change materials used in building wall applications can be either organic materials or inorganic materials.

5.1. Organic PCM

The organic PCM are paraffins, fatty acids and the polyethylene glycol (PEG). They present a congruent phase change, they are not dangerous, and they have a good nucleation rate.

Table 1 presents the thermal properties of organic materials found in the literature, which may be suitable to the specification listed before. T_f is the temperature of fusion, H_f is the latent heat of fusion, C_{p_s} and C_{p_l} are the heat capacities of the solid and liquid phases, k_s and k_l are the thermal conductivities of the solid and liquid phases.

The advantages of organic PCM are:

- availability in a large temperature range,
- freeze without much super cooling,
- ability to melt congruently,
- self-nucleating properties,
- compatibility with conventional material of construction,
- no segregation,
- chemically stable,
- high heat of fusion,
- safe and non-reactive,
- recyclable.

The disadvantages of organic PCM are:

- low thermal conductivity,
- low volumetric latent heat storage capacity,
- flammable (depending on containment).

5.2. Inorganic PCM

The inorganic PCM are salt hydrates. Table 2 lists some inorganic PCM.

The advantages of inorganic PCM are:

- high volumetric latent heat storage capacity,
- low cost and easy availability,

Table 1
Organic PCM in literature (MP: methyl palmitate; MS: methyl stearate; U: unknown; n.a.: not available).

Materials	T_f (°C)	H_f (kJ/kg)	C_{p_s} (kJ/kg/K)	C_{p_l} (kJ/kg/K)	k_s (W/m^2/K)	k_l (W/m^2/K)	References
GR25	23.2–24.1	45.3	1.2	1.2	n.a.	n.a.	[15,16]
PEG600	22	127.2	n.a.	2.49	n.a.	0.189	[15]
n-Octadecane	27	243.5	1.934	2.196	0.358	0.148	[17]
n-Eicosane	37	241	2.01	2.04	0.15	0.15	[17]
P116	47	225	2.4	1.9	0.24	0.24	[17]
Butyl stearate	19	140	n.a.	n.a.	n.a.	n.a.	[18,19]
ERMEST2325	17–20	138	n.a.	n.a.	n.a.	n.a.	[20,21]
RT27	26–28	179	1.8	2.4	0.2	0.2	[22–25]
MICRONAL26	26	110	n.a.	n.a.	n.a.	n.a.	[24,26]
RT20	22	172	n.a.	n.a.	n.a.	n.a.	[27]
MP65%–MS35%	21.8–24.5	175	n.a.	n.a.	n.a.	n.a.	[28]
MP77%–MS23%	22.4–23.8	177	n.a.	n.a.	n.a.	n.a.	[28]
MP93%–MS7%	22.2–22.8	182	n.a.	n.a.	n.a.	n.a.	[28]
GR41	43	63	n.a.	n.a.	0.15	0.15	[29]
GR27	28	72	n.a.	n.a.	0.15	0.15	[29]
Eutectic capric–myristic	21.7	155	n.a.	n.a.	n.a.	n.a.	[30]
MICRONAL 5001	26	110	n.a.	n.a.	n.a.	n.a.	[31]
MICRONAL 5008	22	110	n.a.	n.a.	n.a.	n.a.	[31]
Heptadecane	22	214	n.a.	n.a.	n.a.	n.a.	[32]
MPCM28-D	28	180–195	n.a.	n.a.	n.a.	n.a.	[33]
UNICERE55	45–60	185	n.a.	n.a.	n.a.	n.a.	[19]
n-Nonadecane	31.8	160	n.a.	n.a.	n.a.	n.a.	[34]
Eutectic capric–stearic	24.7	179	n.a.	n.a.	n.a.	n.a.	[35]
Non-eutectic capric–lauric	19.2–20.3	144–150	n.a.	n.a.	n.a.	n.a.	[36]
U3	28	244	n.a.	n.a.	0.28	0.22	[37]
U4	13.6–23.5	104.5–107.5	4	4.1	0.18	0.22	[13,38–41]
RT25	25	147	2.9	2.1	1.02	0.56	[42]

- sharp phase change,
- high thermal conductivity,
- non-flammable.

The disadvantages of inorganic PCM are:

- high volume change,
- supercooling,
- segregation.

6. PCM containment

6.1. The impregnation of building materials

The simplest method consists in the direct impregnation of the PCM into gypsum, concrete or other porous materials to form mixed type PCMIBW. Khudhair and Farid [48] explained the different impregnation techniques. The volume occupied by the PCM in the pores is small enough to prevent from the isolation of the solid PCM crust. The structure of the porous material transports the heat to the pores. Unfortunately, important leakage have been observed, in particular by Xiao et al. [49]. Cabeza et al. [26] also reported an interaction between the PCM and its porous container. This interaction can deteriorate the mechanical properties of the container.

The materials used for impregnation are as follows:

plaster: [18,20,21,28,32,35,36,50–52].
concrete: [19,44,50].
vermiculite: [30].
wood: [53].
cement: [34].
compound: [54–56].

6.2. The micro-encapsulation

The micro-encapsulation consists in enclosing the PCM in a microscopic polymer capsule. The microcapsules form a powder, which is then included in the recipe of a building construction material. Special attention has to be taken in the choice of the capsule's material to avoid chemical reactions between the capsules and the building material. The PCM is trapped and cannot leak anymore, and the size of the capsules is small enough to prevent from a disproportionate isolation of the solid crust of the PCM.

The quality of the process of micro-encapsulation is evaluated by the ratio between the mass of the satisfying capsules (hermetic

Table 2
Inorganic PCM in literature (U: unknown).

Materials	T_f (°C)	H_f (kJ/kg)	C_{p_s} (kJ/kg/K)	C_{p_l} (kJ/kg/K)	k_s (W/m^2/K)	k_l (W/m^2/K)	References
Eutectic salt	32	216					[43]
SP25A8	25–26	180	2.5		0.6	0.6	[23]
Calcium chloride hexahydrate	26–29	175	2.3	1.4	1	1	[25]
Sodium thiosulfate pentahydrate	40–48	210	1.46	2.4			[44]
U1	30–32.5	131					[45,46]
U2	26–28	188	1.44	1.44	1.09	0.54	[47]
$CaCl_2{\cdot}6H_2O$	29.8	191					[37]
S27	27	190	1.5	2.22	0.79	0.48	[42]
L30	30	270	1.23	1.79	1.02	0.56	[42]

capsules containing PCM) and the total mass of the powder. Hawlder et al. [57] investigated the influence on this ratio of several parameters such as the duration of the process, the quantity of PCM and reticulation agent introduced in the solution, for a coacervation micro-encapsulation.

Three characteristics of the capsules are relevant to appreciate the quality of the powder: their mean diameter, the thickness of their shell, the mass percentage of PCM compared to the total mass of the capsule. For an in situ polymerization, Zhang et al. [58] varied the strength of the beater, which caused a variation in the mean size of the capsules. Sarier and Onder [59] performed a statistical study on the size of the capsules to evaluate their degree of inhomogeneities in a powder.

The PCM powder has to be included into the mixture of a building material, such as concrete, a polymer or gypsum, to form the improved building phase change material. Thus, the thermal behaviour of the PCMIBW depends on the thermal specifications of the building material.

However, DSC measurements have been performed directly on the PCM powder to determine its specific latent heat and its temperature of fusion. Yamagishi et al. [60] observed a supercooling effect during the solidification of microencapsulated. When the size of the microcapsules decreases below a few microns, the nucleation agents, which are necessary to the start of the solidification, rarefy. The solidification is delayed. Zhang et al. [58] attenuated the supercooling effect by adding nucleation agents into the PCM. The nucleation agent, which they used, was 1-tetradecanol for C_{14} PCM, and 1-pentadecanol for C_{15} PCM.

In the literature review, about 20 papers deals with microencapsulated PCM in building material, most of them being plaster material. For example, Schossig et al.. [61] built gypsum boards containing microencapsulated PCM, of which the temperature of fusion was around 25 °C. Fig. 15 is a SEM photography of the PMC in the concrete.

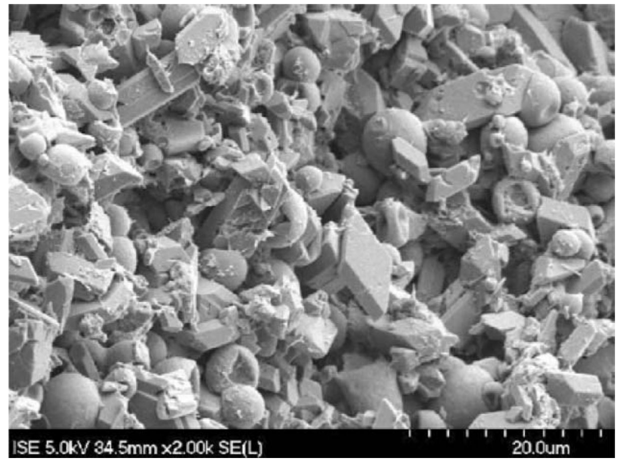


Fig. 15. SEM photography of a concrete wall containing microencapsulated PCM, from Schossig et al.. [61].

6.3. Shape-stabilized PCM

Shape-stabilized PCM are prepared from a liquid mixture of the PCM and a supporting material. The mixture is then cooled below the glass transition temperature of the supporting material, until it becomes solid. An appropriate choice of the supporting material allows PCM mass proportions up to 80%. Fig. 16 shows two pictures of a plate made of shape-stabilized PCM. On the first one, one can notice that the shape-stabilized PCM looks like a homogeneous material. The second picture shows the microstructure of the material.

The most common supporting materials found in the literature are high-density polyethylene (HDPE) and styrene–butadiene–styrene (SBS). Sari [62] did not observe any leakage of the phase change material by using HDPE as supporting material. Xiao et al. [49] made the same remark for SBS. Zhang et al.. [56] report that the PCM mixes better into SBS than HDPE, but the shape-stabilized PCM is more rigid when using HDPE.

The thermal conductivity of a shape-stabilized PCM is not very high, which is a problem in latent heat storage systems. Thus, researchers added some materials into their shape-stabilized PCM composition to improve their conductivity. The most complete study on those additives has been made by Zhang et al. [63]. They found that most efficient conducting material was ex-foliated graphite. The conductivity of their shape-stabilized PCM evolved from 0.150 W/mK to 0.229 W/mK by adding 10% weight graphite into the mixture. Zhang et al.. [63] developed a model to predict the thermal conductivity of the material from its composition.

6.4. Other containers

Other containers can also be used for the integration of PCM in building walls. Ahmad et al. [15,16] used PVC panels filled with PCM. Carbonari et al. [43] used sandwich panels with plastic rigid containers of PCM. Castell et al. [23] used CSM panels. Konuklu and Paksoy [31] tested aluminium foils to incorporate PCM in a multi-layers panel. Medina et al. [45], Voelker et al. [37], Zhang et al. [46] and Guceri and Faunce [64] filled tubes with PCM that was integrated in the wall. Pasupathy et al. [47] filled a steel container with PCM for being included in the roof slab.

7. Measurement of the thermal properties of PCM and PCMIBW

Arkar and Medved [65] and Cho and Choi [66] showed that a perfect knowledge of the thermal properties of the PCM and the

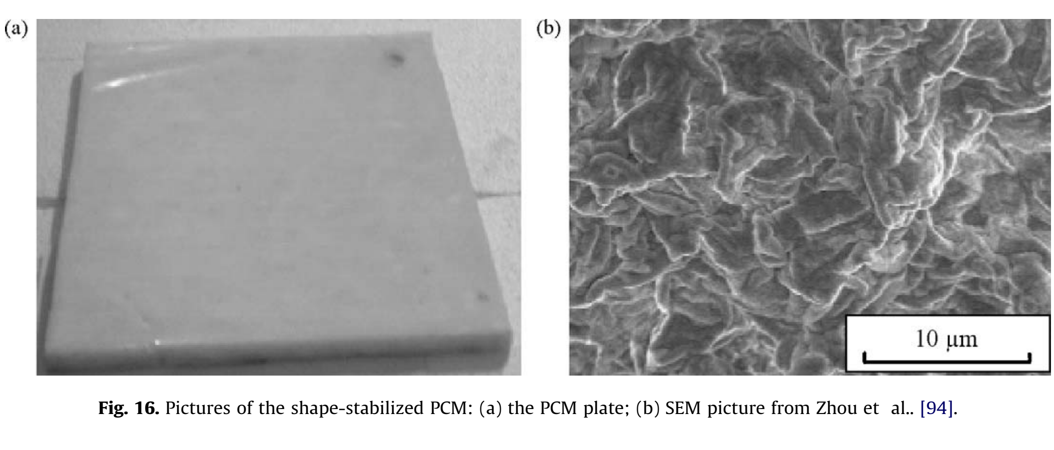


Fig. 16. Pictures of the shape-stabilized PCM: (a) the PCM plate; (b) SEM picture from Zhou et al.. [94].

way those properties are measured, is necessary to correctly analyze a latent heat storage system. Tyagi and Buddha [8] warn the reader about data provided by the manufacturer, which could be erroneous (usually over optimistic). Thus, measurement methods have been developed in order to get the thermodynamic characteristics of PCMs. Even if several measurement methods exist, the differential scanning calorimetry (DSC) is the most common one.

7.1. DSC: differential scanning calorimetry

This measurement method has been initially developed to characterize the heat exchanges between some materials and their environment during transformations such polymerization or phase change of polymers. The name differential scanning calorimetry is very explicit:

- *Calorimetry*: the calorimetry is the measurement of the quantity of heat that can be absorbed or released by a body subjected to a change of temperature. In our case, the heat transfer is due to conduction.
- *Differential*: the measurement setup is designed to have two different samples in identical conditions. The thermal reaction of the sample to characterize is obtained by comparison with the thermal reaction of the reference sample (which properties are known).
- *Scanning*: the thermal excitation is a ramp of temperature. The temperature rate has to be determined by the researcher.

Two kinds of DSC setups exist. The power compensation DSC consists in two independent calorimeters. The heat flux DSC has got a Siamese structure: the two samples are connected to the same metal disc; the behaviour difference of the samples submit to the same temperature excitation leads to a voltage difference between the samples; the absorbed heat in the PCM sample is deduced from the voltage.

The weight of DSC measurement sample is only a few grams. Thus, DSC provides information about the local properties of the material. It does not characterize the thermal behaviour of the bulk BIPCM and then this method is useful when the composite PCM characteristic size can be tested.

The Annex 17 of ECES (International Energy Agency) [67] observed the response of several samples with different masses, to a temperature scanning with different rates. The material of the sample did not suffer from super cooling. Results are shown in Fig. 17. The equivalent heat capacity calculated using the DSC curves is clearly influenced by the sample mass and heating rate.

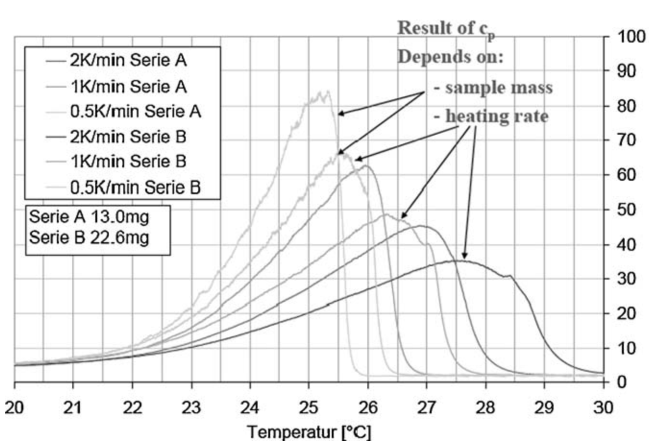


Fig. 17. Temperature scanning responses depending on sample mass and heating rate from [67].

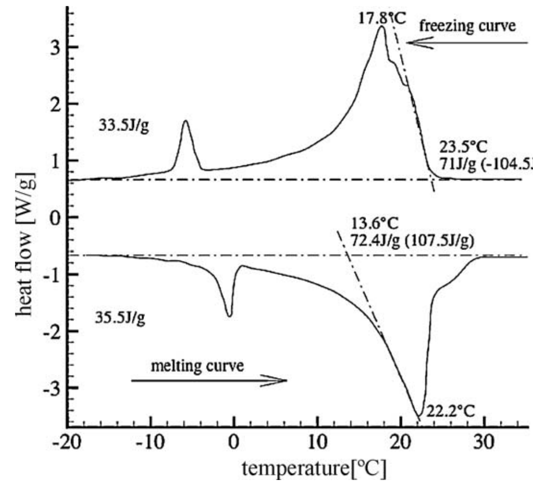


Fig. 18. Differential scanning calorimeter melting and freezing curves for the composite PCM from [39].

The DSC is a complex system and the direct use of the measured curves is not physically correct because some heat transfer phenomena are omitted: the convection in the sample (i.e. capsule), the non-uniformity of the temperature in the sample (conduction), the time needed to heat or cool the sample (inertia). An inverse method based on this physical phenomenon is necessary to qualitatively enhance the results of DSC.

Fig. 18 from [39] shows the DSC curves obtained for a paraffin mixture. The heating and cooling curves are of course different and the melting and freezing temperatures are 13.6 °C and 23.5 °C, respectively. The mixture phase change depends on the phase diagram but the DSC curves are not sufficient to get it. Further investigations are needed to calculate, from DSC, the physical characteristics needed to model the phase change of such PCM mixture.

7.2. The T-history method

The T-history method has been designed to test large samples. It also provides information about the thermal conductivity of the PCMIBW, and allows to test several samples at the same time.

The method is explained by Yinping and Yi [68]: samples of PCMIBW are put in different vertical tubes; a reference material is also put in a vertical tube. The temperature of the sample is measured with a thermocouple located at the center of the tube. At the beginning of the test, all the materials are in the liquid phase. The tubes are suddenly immersed into a controlled atmosphere (usually cold water), in which the temperature is regulated and is below the fusion temperature of the PCMIBW. The temperature inside each tube and in the controlled atmosphere is monitored; an example of the curve obtained is shown in Fig. 19.

A convective coefficient is deduced from the temperature curve of the reference material. Three steps appear in the temperature curve of the PCMIBWs: the cooling of the liquid phase, the solidification of the PCM, and the cooling of the solid phase. The latent heat of the material and the heat capacity of its different phases are obtained after the calculation of the areas between the sample temperature curve and the atmosphere temperature curve (A1, A2 and A3) for each step. The thermal conductivity of the sample is obtained by using an inverse method on the total solidification time.

The method was improved by Marin et al. [69] to obtain the heat capacity as a function of the temperature. Peck et al. [70] proposed to lie the tubes horizontally in order to minimize disparities of the heat flux on their surface.

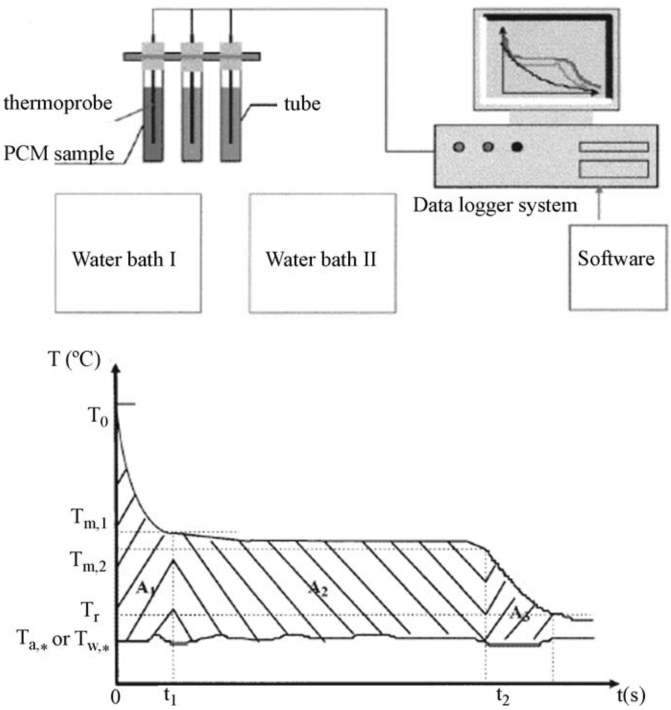


Fig. 19. T-history experimental setup and T-history temperature curves.

7.3. The guarded hot-plate setup

Darkwa and Kim [71] used the guarded hot-plate to compare the storage performances of two different PCM wallboards. The setup contained a stack composed of a cold source, a hot source, a heat flux meter and the wallboard sample. The stack is isolated on every side. Fig. 20 shows the setup. The specificities of the wallboard sample are obtained by the integration of the measured heat flux during the phase change.

Schossig et al. [61] also designed a guarded hot-plate type measurement setup. The stack was composed of the wall sample and one copper plate on each side.

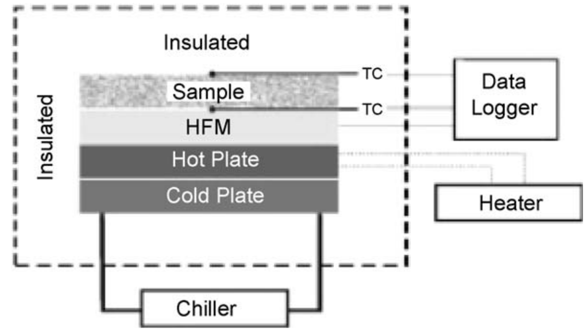


Fig. 20. The measurement setup from the Darkwa et al. [71].

8. Experimental studies

Table 3 summarizes the experimental studies concerning measurements held in a room with walls containing PCM. Most of these experiments were carried out in outdoor conditions with no internal gains due to occupation (i.e. real use of the building). The phase change temperature of the materials tested varies between 20 °C and 30 °C, which is the usual thermal comfort zone of buildings. The PCM are mainly contained in plasterboards.

In the majority of the experimental studies, the measurements concern the air temperature in the test cell (usually one point) and, sometimes, the walls temperature. In all the cases, the major effect of PCMIBW is to reduce the temperature fluctuations with a more or less important time lag concerning the temperature maximum. There are few studies with heat flux measurements whereas it is an interesting way to calculate the thermal energy stored/release. On the whole, there is a lack of indicators allowing evaluating the real effectiveness of the solutions tested.

The thermal comfort of occupants is driven in particular by the air temperature (convective heat transfer) and the surface temperature using the mean radiant temperature (radiative heat transfer). A special attention must be paid to these two parameters to really assess the effect of PCM on thermal comfort.

Concerning the energy, Castell et al. [23] measured a reduction of about 15% of electricity consumption during summer 2008. A more systematic study of energy reduction coupled with life cycle analysis is necessary to really assess the performance of PCMIBW.

Table 3
Experimental studies involving PCM wallboards; the material refers to Tables 1 and 2.

Ref.	Material	Container	Cell size	Number of cells	Conditions
[16]	PEG600	PVC panel	0.9 m × 0.9 m × 0.9 m	2	Outdoor
[18]	Butyl stearate	Gypsum	2.88 m × 2.22 m × 2.24 m	1	Outdoor
[20]	Butyl stearate palmitate; ERMEST2325	Gypsum	2.27 m × 2.29 m × 2.45 m	2	Laboratory
[26]	MICRONAL26	Gypsum	2.4 m × 2.4 m × 2.4 m	2	Outdoor
[43]	Eutectic salt	Sandwich panel	4.37 m × 3.39 m × 2.7 m	1	Laboratory
[23]	RT25; SP25A8	CSM panel	2.4 m × 2.4 m × 2.4 m	2	Outdoor
[24]	MICRONAL26; RT27		2.4 m × 2.4 m × 2.4 m	2	Outdoor
[27]	RT20	Gypsum	0.7 m × 0.7 m × 0.7 m	3	Laboratory
[72]	RT20	Gypsum	0.7 m × 0.7 m × 0.7 m	3	Laboratory
[31]	PC5001; PCM5008	Aluminium foils	2.7 m × 2 m × 1.5 m	3	Outdoor
[38,39]	U4	ENERGAIN	3.1 m × 3.1 m × 2.5 m	1	Laboratory
[40]	U4	ENERGAIN	0.5 m × 0.5 m × 0.5 m	2	Laboratory
[53,56]	Paraffin	Shape-stabilized	0.575 m × 0.453 m × 0.463 m	1	Outdoor
[54]	Paraffin	Shape-stabilized	3 m × 2 m × 2 m	1	Outdoor
[41]	U4	ENERGAIN	4 m × 3 m × 2.5 m	1	Laboratory
[45,46]	U1	Tube	1.83 m × 1.83 m × 1.22 m	2	Outdoor
[47]	U2	Steel	1.22 m × 1.22 m × 1.44 m	2	Outdoor
[21]	ERMEST2325	Gypsum	2.27 m × 2.29 m × 2.45 m	2	Laboratory
[61]		Gypsum	Room of a building	2	Outdoor
[36]	Capric–lauric non-eutectic	Gypsum	5 m × 3.3 m × 2.8 m	1	Outdoor
[37]	U3; $CaCl_2{\cdot}6H_2O$	Gypsum; tube	2.95 m × 4.43 m × 2 m	2	Outdoor

9. Numerical studies

The phase change can be taken into account in the heat equation using either the effective heat capacity method or the enthalpy method. These two methods have been extensively studied in the literature, for example: [73–75] for the effective heat capacity method and [76–78] for the enthalpy formulation method. The two methods have the advantages of allowing using one formulation of the heat equation for the entire domain and of avoiding solving the melting front position.

The numerical studies involving PCM integrated in building walls can be roughly categorized as follows:

- unidirectional heat equation in a single wall: [13,15,32,38,42, 47,71,79–86].
- two-dimensional heat equation in a single wall: [17,43,87].
- unidirectional heat equation in the wall, energy balance in a room: [40,53,88–96].
- two- or three-dimensional heat equation in the wall, energy balance in a room: [16,97].

Most of the studies concerning unidirectional heat equation in a building wall with PCM deal with the problem of PCM optimization: phase change temperature, position of the PCM, thickness. One of the most important features is the thickness of the PCM wall: the more the wall is thick, the more the price of the construction is high. Of course, when the thickness is large, the time needed for the heat to penetrate the PCM becomes larger than 12 h and the storage process cannot be complete during a day [13]. This optimal thickness depends on the diffusivity of the medium and then must be held for each PCMIBW.

The unidirectional conductive heat transfer in walls is a common assumption in building simulation. In low energy building, this assumption is no more realistic and then attention must be paid in future studies concerning this assumption especially for thermal bridges reduction.

The heat transfer between the PCM wall and the air is due to convection. For external walls surface, the convective heat transfer is driven by forced convection, but as the walls are insulated, this transfer process is not prevalent. The convective heat transfer between the internal face of the wall and the indoor air is important to evaluate the store/release process in PCM. Liu and Awbi [41] found that the correlation used to evaluate the convective heat transfer for ordinary walls underestimate this coefficient for PCM wall (by a factor of 2 in their experiment). This is a very important problem because there is a lack of knowledge concerning the convective heat transfer with PCM walls whereas numerical simulations need the convective heat transfer value!

Most of the studies deal with non-occupied rooms. Of course, the evaluation of air temperature in a building is clearly affected by internal heat loads. One way to evaluate the optimum phase change temperature is to calculate the thermal evolution of a building without PCM and calculate the mean surface temperature of the walls for the storage period. This optimization can only be done if internal loads due to occupation are taken into account with realistic scenario.

10. Conclusions

This paper is the state of the art of phase change material integrated in building walls. All of the PCM reviewed have a good potential for reducing cooling loads by enhancing the storage capacity of the building envelope. However, this storage capacity can be enhanced with an increase of the PCMIBW thermal conductivity.

From a practical point of view, a more systematic evaluation of the various PCM integrated in the building structure is needed, in particular in real use condition. Such analysis can be numerical but attention must be paid to numerical modelling assumptions: convective heat transfer coefficient, use of the phase diagram. Moreover, there is a lack of clear indicator to effectively assess the PCMIBW.

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